Photocycloaddition reactions of 2-acylcyclohex-2-enones

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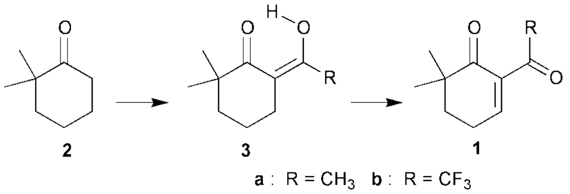
The newly synthesized 2-acylcyclohex-2-enones 1 photocycloadd selectively to the C–C triple bond of 2-methylbut-1-en-3-yne giving diacylcyclobutene derivatives 4 and 5, and they react with 2,3-dimethylbut-2-ene in an overall [4+2]-photocycloaddition to afford benzopyranones 7.

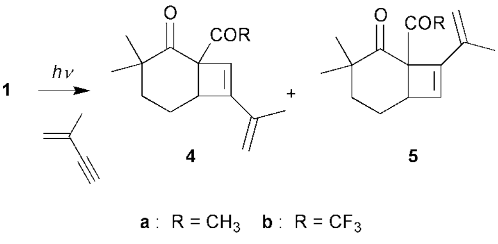
We have recently published results[1,2] on the photocycloaddition of cyclohex-2-enones to 2-methylbut-1-en-3-yne, showing that the substitution pattern on C(2) of the enone has a pronounced influence on the outcome of the reaction. While the (parent) cyclohex-2-enone affords mainly bicyclo[4.2.0]octan-2-ones resulting from [2 + 2]-cycloaddition to the C–C double bond of the enyne, 2-alkylcyclohex-2-enones give naphthalen-1(2*H*)-ones *via* 1,6-cyclization of the triplet biradical intermediate. Finally, 2-cyanocyclohex-2-enone yields a mixture of these two types of compounds and, in addition, one product resulting from cycloaddition to the C–C triple bond of the enyne. Here we report on the synthesis of the hitherto unknown 2-acylcyclohex-2-enones **1a** and **1b** and on their unprecedented behaviour on irradiation in the presence of this same enyne or of 2,3-dimethylbut-2-ene, respectively. *C*-Acylation of 2,2-dimethylcyclohexanone (**2**)[3] with either LDA–acetyl cyanide or NaOMe–ethyl trifluoroacetate affords 2-(1-hydroxyethylidene)-6,6-dimethylcyclohexanones **3a** and **3b** in 60 and 62% yield, respectively.[4] Dehydrogenation to **1a** and **1b** is then achieved by treatment[5] of **3** with PhSeCl and then H_2O_2 in 96 and 90% yield, respectively (Scheme 1).[6–8]



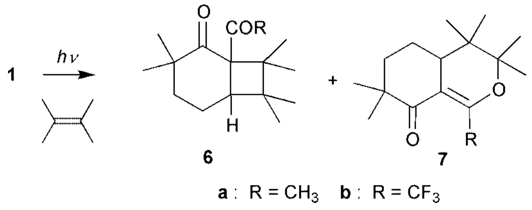
Scheme 1

Monitoring the irradiation (λ > 340 nm) of an argon-degassed solution of **1a** (0.1 M) and 2-methylbut-1-en-3-yne (1 M) in benzene by GC indicates the formation of two new products, **4a** and **5a**, in a 1 : 1 ratio. At degrees of conversion of **1a** higher than 40–45% the photoproducts start to undergo secondary reactions. Under the same conditions **1b** gives a 2 : 3 mixture of **4b** and **5b**. In preparative runs[9] the photoproducts were separated, isolated and identified as being regioisomeric 1-acylbicylo[4.2.0]oct-7-en-2-ones (Scheme 2).[10]

Similarly, monitoring the irradiation of **1** in the presence of a tenfold molar excess of 2,3-dimethylbut-2-ene in benzene indicates the formation of two new products **6** and **7**, in a 3 : 1 ratio from **1a** and in a 2 : 1 ratio from **1b**, the major products **6** again undergoing consecutive photoreactions. After isolation as above[9] the major products **6** turned out to be (the expected) 1-acylbicyclo[4.2.0]octan-2-ones—which then undergo α-cleavage to afford aldehydes—while the minor products **7** were identified as being 3,4,4a,5,6,7-hexahydro-8*H*-isochromen-8-ones (Scheme 3).[11]



Scheme 2



Scheme 3

The behaviour of **1a** and **1b** contrasts that of 6,6-dimethyl-2-pivaloylcyclohex-2-enone[12] which on the one hand is thermally more stable, *i.e.* it does not enolize, but on the other hand does not photocycloadd to alkenes or enynes, most probably because of the (steric) bulk of the *tert*-butyl substituent. Despite their pronounced lack of (thermal) stability, which can nevertheless be controlled by careful handling,[5,13] 2-acylcyclohex-2-enones **1a** and **1b** turn out to be remarkable substrates for intermolecular photocycloaddition reactions *a*) due to the fact that on reaction with the enyne excited cyclohexenones **1** give (novel) cyclobutene adducts selectively, thus corroborating the assumption[2] that the amount of this type of cycloadduct will increase with decreasing reduction potential of the (excited) enone, and *b)* because photochemical [4 + 2]-cycloadditions of s-*cis* enones to alkenes to give dihydropyrans have not been reported so far in the literature. Further studies aiming at the improvement in the product ratio pyran *vs.* cyclobutane are in progress.

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Notes and references

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2 B. Witte, L. Meyer and P. Margaretha, *Helv. Chim. Acta*, 2000, **83**, 554.
3 R. Z. Andriamialisoa, N. Langlois and Y. Langlois, *Tetrahedron Lett.*, 1985, **26**, 3563.
4 **3a**: δ_H(500 MHz, $CDCl_3$) 16.27 (O**H**), δ_C(125 MHz, $CDCl_3$) 199.4, 188.1, 105.4 (sp^2 C-atoms); **3b**: δ_H(500 MHz, $CDCl_3$) 15.53 (O**H**), δ_C(125 MHz, $CDCl_3$) 195.8, 179.5 (q, J_{CF} = 33.9 Hz), 103.4 (sp^2 C-atoms). Both **3a** and **3b** gave satisfactory elemental analyses.
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6 Both compounds **1** are sensitive to acids and bases in undergoing irreversible (*cf.* ref. 5) enolization to 2-(1-hydroxyethylidene)-6,6-dimethylcylohex-3-en-1-ones.
7 In the normal (ref. 5) work-up trifluoroacetylcyclohexenone **1b** is obtained in a mixture with its hydrate, *i.e.* 2-(1,1-dihydroxy-2,2,2-trifluoroethyl)-6,6-dimethylcyclohex-2-enone; pure **1b** is obtained by azeotropic removal of water by distillation of added benzene.

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8 **1a**: light yellow liquid, δ_H(500 MHz, C_6D_6) 7.13 (t, J = 4 Hz), 2.41 (s, 3H), 1.65 (dt, J = 4 and 6 Hz, 2H), 1.18 (t, J = 6 Hz, 2H), 0.88 (s, 6H), δ_C(125 MHz, C_6D_6) 201.4, 197.6, 153.6 (**C**H), 138.0, 42.1, 35.7 (**C**H_2), 30.7 (**C**H_3), 24.1 (**C**H_3), 23.4 (**C**H_2); **1b**: light yellow liquid, δ_H(500 MHz, C_6D_6) 7.31 (t, J = 4 Hz), 1.81 (dt, J = 4 and 6 Hz, 2H), 1.29 (t, J = 6 Hz, 2H), 0.96 (s, 6H), δ_C(125 MHz, C_6D_6) 199.5, 184.8 (q, J_{CF} = 37.5 Hz), 156.3 (**C**H), 135.2, 126.6 (q, J_{CF} = 290 Hz), 42.2, 35.5 (**C**H_2), 23.7 (**C**H_3), 23.6 (**C**H_2).

9 *Preparative Details*: an argon degassed solution of **1** (1 mmol) and enyne/alkene (0.01 mol) in benzene (10 ml) is irradiated with a 250 W mercury lamp using a liquid filter with cutoff $<$ 340 nm for 24 h up to a degree of conversion of **1** of 40–45%. After evaporation of the solvent the residue is chromatographed (SiO_2, pentane–ether 9 : 1). The orders of elution are **4a** $<$ **5a**, **5b** $<$ **4b**, **6a** $<$ **7a** and **6b** $<$ **7b**, the enones **1** always having much lower R_f values. The new compounds **4**, **5**, **6** and **7**—all colourless liquids—have been fully characterized and have spectroscopic properties compatible with the structures assigned.

10 **4a**: δ_H(500 MHz, C_6D_6) 5.90 (s), 4.92 (s), 4.89 (s) (olefinic H-atoms), δ_C(125 MHz, C_6D_6) 211.4, 204.3, 153.7, 137.5, 128.1 (**C**H), 115.7 (**C**H_2) (sp^2 C-atoms); **5a**: δ_H(500 MHz, C_6D_6) 5.81 (s), 5.71 (s), 5.08 (s) (olefinic H-atoms), δ_C(125 MHz, C_6D_6) 212.0, 203.7, 148.0, 135.6, 134.2 (**C**H), 117.7 (**C**H_2) (sp^2 C-atoms); **4b**: δ_H(500 MHz, C_6D_6) 5.80 (s), 4.90 (s), 4.81 (s) (olefinic H-atoms), δ_C(125 MHz, C_6D_6) 211.1, 189.7 (q, J_{CF} = 35 Hz), 154.2, 137.0, 123.7 (**C**H), 117.1 (**C**H_2) (sp^2 C-atoms); **5b**: δ_H(500 MHz, C_6D_6) 5.60 (s), 5.40 (s), 4.93 (s) (olefinic H-atoms), δ_C(125 MHz, C_6D_6) 212.4, 190.2 (q, J_{CF} = 34 Hz), 144.3, 135.6, 133.6 (**C**H), 117.9 (**C**H_2) (sp^2 C-atoms).

11 **7a**: δ_C(125 MHz, C_6D_6) 204.3, 161.0, 109.2, 81.4, 43.4 (**C**H), 43.0, 38.4 (**C**H_2), 36.1, 20.2 (**C**H_2) and seven signals for **C**H_3; **7b**: δ_C(125 MHz, C_6D_6) 203.6, 142.5 (q, J_{CF} = 26.3 Hz), 123.0 (q, J_{CF} = 275 Hz), 119.1, 83.1, 45.4 (**C**H), 45.0, 38.9 (**C**H_2), 36.3, 20.6 (**C**H_2) and six signals for **C**H_3.

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